

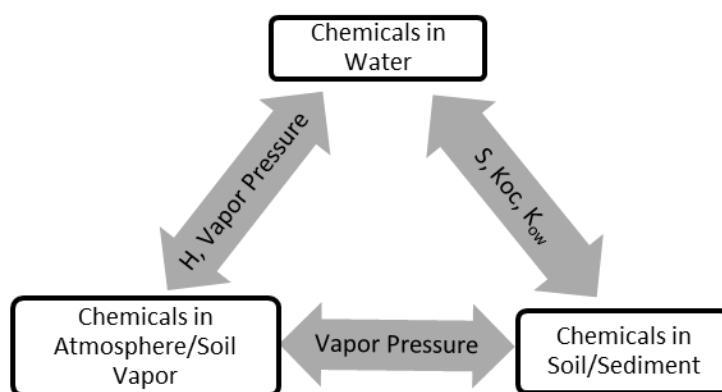
## APPENDIX J

### CHEMICAL PROPERTIES AND PERSISTENCE OF COPCS

The purpose of this appendix is to provide additional information related to the fate and transport of constituents of potential concern (COPC) for the North Branch of the Chicago River North Branch Site Operable Unit (OU) 2. This appendix provides details regarding the physiochemical properties that govern the fate and transport of COPCs and presents a discussion of their impacts to each COPC.

#### 1.0 PHYSIOCHEMICAL PARAMETERS

The fate and transport of chemicals depends on these physiochemical properties: density, water solubility, organic carbon-water partitioning coefficient ( $K_{oc}$ ), octanol-water partitioning coefficient ( $K_{ow}$ ), vapor pressure, and Henry's Law constant (HLC). The following diagram illustrates the relationship between chemicals in different environmental media and the properties that govern the transfer between them.



#### 1.1 Density

Density is defined by USEPA as “a measure of how heavy a specific volume of a solid, liquid, or gas is in comparison to water, depending on the chemical.” (USEPA 2009). In general, if a substance has a density of less than 1.0 grams per cubic centimeter (g/cm<sup>3</sup>) it will float on water while if it has a density of greater than 1.0 g/cm<sup>3</sup> it will sink in water.

#### 1.2 Water Solubility

“The solubility of a chemical in water may be defined as the maximum amount of the chemical that will dissolve in pure water at a specified temperature. Above this concentration, two phases will exist if the organic chemical is a solid or a liquid at the system temperature: a saturated aqueous solution and a solid or liquid organic phase. Aqueous concentrations are usually stated in terms of weight per weight (parts per million [ppm], parts per billion [ppb], grams per kilogram [g/kg], etc.) or weight per volume (milligrams per liter [mg/L], moles per liter [moles/L], etc.).” (Lyman et. al 1990) Chemicals with lower water solubility are more likely to transfer from surface water or groundwater to sediment and soil, and therefore become less mobile. If a chemical is water-soluble, it can leach from soil and is likely to be biodegraded by soil microbes. Lower water solubility of chemicals prevents transport of the chemical. Water solubility is used to estimate the tendency of chemicals to dissolve in groundwater and surface water.

#### 1.3 Organic Carbon-Water Partitioning Coefficient ( $K_{oc}$ )

$K_{oc}$  is “the ratio of the amount of chemical adsorbed per unit weight of organic carbon (OC) in the soil or sediment to the concentration of the chemical in solution at equilibrium” (Lyman et. al 1990).

The common unit of  $K_{oc}$  is liters per kilogram (L/kg). Water is a polar molecule and many organic compounds in soil or sediments are non-polar, making them hydrophobic. Hydrophobic organic chemical pollutants tend to sorb to organic carbon in soil and sediment. The  $K_{oc}$  of an organic compound is related to its water solubility.

Organic compounds with higher values of  $K_{OC}$  (lower water solubility) tend to adsorb to soil and sediment matrices rather than dissolving into groundwater or surface water. Consequently,  $K_{OC}$  is often applied to estimate the extent of the sorption of chemicals in the environment (USEPA 2009).

#### 1.4 Octanol-Water Partitioning Coefficient (K<sub>OW</sub>)

“A coefficient representing the ratio of the solubility of a compound in octanol (a non-polar solvent) to its solubility in water (a polar solvent). The higher the  $K_{OW}$ , the more non-polar the compound. Log  $K_{OW}$  is generally used as a relative indicator of the tendency of an organic compound to adsorb to soil. Log  $K_{OW}$  values are generally inversely related to aqueous solubility and directly proportional to molecular weight.” (USEPA 2012).  $K_{OW}$  can be used to estimate how likely chemicals will partition out of surface water and groundwater into soil and sediment containing hydrophobic constituents.

If the  $K_{OW}$  value of a chemical is less than  $10^2$ , the chemical is not expected to partition into or tend to accumulate in any hydrophobic substance, whereas chemicals with a  $K_{OW}$  value greater than  $10^6$  are likely to accumulate in to hydrophobic substances such as soil and sediments (USEPA 1979).

#### 1.5 Vapor Pressure

Vapor pressure is defined by USEPA as “the force per unit area exerted by a vapor in an equilibrium state with its pure solid, liquid, or solution at a given temperature. Vapor pressure is a measure of a substance's propensity to evaporate. Vapor pressure increases exponentially with an increase in temperature.” (USEPA 2012).

Chemicals with higher values of vapor pressure are more likely to escape from liquid or solid, such as groundwater or soil, into a gaseous form in soil vapor or the atmosphere. Chemicals with a low vapor pressure tend to stay dissolved in water if they are water soluble, and accumulate in soil or biota if they are not water soluble.

#### 1.6 Henry's Law Constant

Henry's Law constant (HLC) is “the ratio of the concentration of a compound in air (or vapor) to the concentration of the compound in water under equilibrium conditions” (USEPA 2012).

There are two expressed equations of HLC (USEPA 2009):

$$\text{Conventional HLC} = \frac{\text{Vapor Pressure} \times \text{Molecular Weight}}{760 \times \text{Water Solubility}},$$

Where vapor pressure is expressed as torr, molecular weight is expressed in g/mole, and water solubility is expressed in mg/L.

And

$$K_{AW}(\text{Dimensionless HLC}) = \frac{\text{Chemical's Concentration in Gas Phase}}{\text{Chemical's Concentration in Liquid Phase}} = \text{HLC}/RT$$

Where R is the ideal gas constant of  $8.206 \times 10^{-5}$  atm-m<sup>3</sup>/K-mole, and T is absolute temperature expressed in Kelvin (K).

HLC can be expressed in dimensionless form or with units such as atm-m<sup>3</sup>/mol and pa-m<sup>3</sup>/mol.

HLC is related to the transport process of chemicals from a liquid into air. Chemicals with a high value of HLC tend to volatilize from water to air whereas chemicals with a low HLC tend to stay in water or be adsorbed onto soil or sediment. Since vapor pressure and solubility of chemicals are subject to temperature, Henry's law constant changes with temperature.

## 2.0 CONTAMINANT PERSISTENCE

A chemical's persistence in the environment is affected by the following mechanisms: volatilization, sorption, biodegradation, advection, dispersion, and diffusion. These mechanisms are described in this section.

### 2.1 Volatilization

"Volatilization is the process of transfer of a chemical from the aqueous or liquid phase to the gas phase." (USEPA 2012).

Temperature affects volatilization in several ways, since the factors that affect the volatilization process, such as vapor pressure and Henry's law constant, are also temperature-dependent. Other factors, such as solubility, molecular weight, chemical concentration, and the nature of the gas-liquid interface, also affect the rate of volatilization. In general, higher temperature increases volatilization rate. Chemicals with lower solubility are more likely to stay on the water-atmosphere surface and, therefore, the volatilization will be increased. The larger molecular weight a chemical has, the slower its volatilization process tends to happen. In addition, chemical structure of the contaminant will also affect the volatilization, because chemical structure of the contaminant will affect the bonds between the chemical and water molecule.

### 2.2 Sorption

USEPA defines sorption as "the interaction of a contaminant with a solid, including adsorption and absorption processes, where adsorption refers to an excess contaminant concentration at the surface of a solid while absorption implies a more or less uniform penetration of the solid by a contaminant" (USEPA 2012).

Partition coefficient  $K_p$  can be applied to express sorption the process (USEPA 1990).

$$K_p = \frac{C_s}{C_w} = K_{oc} \times f_{oc}, \quad \left( \frac{L}{kg} \right)$$

Where,

$C_s$  – Concentration of the contaminant in solid phase

$C_w$  – Concentration of the contaminant in solution phase

$K_{oc}$  – Organic Carbon-Water Partitioning Coefficient

$f_{oc}$  – Organic carbon fraction

Sorption can be affected by properties of the contaminants, such as water solubility, polar/ionic character, and octanol/water partition coefficient. Soil characteristics, including mineralogy, permeability/porosity, texture, surface charge, organic carbon content, and surface area, will also exert an influence on sorption process. In addition to soil characteristics and contaminant properties, surface/ground water characteristics such as pH of the water, salt content, and dissolved organic carbon content will also influence the sorption process.

Adsorption should be taken into account when estimating the amount of a contaminant at a site, as well as the time required for a contaminant transport from one point to another.

### 2.3 Biodegradation

USEPA defines biodegradation as "a process by which microbial organisms transform or alter (through metabolic or enzymatic action) the structure of chemicals introduced into the environment." (USEPA 2012).

Biodegradation can take place over a wide range of temperatures, although decreasing temperatures correlates with decreasing biodegradation rate. In general, chemicals with lower molecular weight are more likely to be biodegraded by microbes than those with larger molecular weight. The biodegradation rate will be enhanced if enough nutrients, including nitrogen, phosphorus, and potassium (NPK), are provided to local microbes. Soil moisture can provide water to biodegradation process, which is critical for bacterial metabolism, so soil moisture will also exert an influence on biodegradation. (U.K. Environment Agency 2013).

Biodegradation of contaminants is influenced by the geologic and chemical characteristics of the site.

All the geologic and chemical indicators are grouped into three categories for discussion to assess the biodegradation of the contaminants.

- **Electron Acceptors** - Electron acceptors include dissolved oxygen, nitrate, and sulfates. These compounds are utilized by microbes during biodegradation process and contaminants such as VOCs and PAHs provide a demand for electron acceptor (WDNR 2014). Therefore, increasing trends of oxygen, nitrate and/or sulfate can relate to the occurring of biodegradation process within the dissolved plume. The lower the oxidation reduction potential indicates the greater the potential for a reducing and anaerobic environment. When the parameters regarding electron acceptors from up gradient wells and plume wells are evaluated and compared with each other to identify positive indications for microbial activity and biodegradation within the plume, it is found that DO, nitrate, sulfate, and ORP values are all lower within the plume indicating biodegradation is occurring under reducing environment with anaerobic degradation.
- **Metabolic Byproducts** - Dissolved manganese ( $Mn^{2+}$ ), dissolved iron ( $Fe^{2+}$ ), and methane are byproducts of microbial metabolism and may increase within the dissolved plume due to biodegradation process of microbes (WDNR 2014). If iron and manganese are reduced, their concentrations in groundwater will increase, as the reduced forms of these compounds have greater solubility than do the oxidized forms. Methane concentrations will increase as methanogenesis occurs. After the evaluation and comparison of the dissolved manganese and dissolved iron in upgradient wells and plume wells, it is found that iron, manganese and methane concentrations are all higher within the plume, suggesting biodegradation is occurring through methanogenesis within the plume.
- **Alkalinity** - Alkalinity will increase with increased carbon dioxide ( $CO_2$ ) released during biodegradation as the end product. Alkalinity is expected to increase within the plume when biodegradation occurs. Alkalinity values in up gradient wells and plume wells shows that alkalinity is higher within the plume than in the upgradient wells which indicates biodegradation is occurring within the plume.

## 2.4 Advection, Dispersion, and Diffusion

Advection, dispersion, and diffusion are the processes that may increase the spreading of contamination in groundwater.

Advection is defined by USEPA as “bulk transport of the mass of discrete chemical or biological constituents by fluid flow within a receiving water. Advection describes the mass transport due to the velocity, or flow, of the water body” (USEPA 2012). Advection processes can be affected by aquifer properties, especially hydraulic conductivity, effective porosity, and hydraulic gradient, and are independent of contaminant properties. It is the primary mechanism driving contaminant movement in the subsurface.

Dispersion is defined by USEPA as “the spreading of chemical or biological constituents, including pollutants, in various directions from a point source, at varying velocities depending on the differential in-stream flow characteristics” (USEPA 2012). Dispersion is dependent on aquifer properties and independent of contaminant properties. Dispersion process can cause longitudinal, transverse, and vertical spreading of a plume and reduce contaminant concentrations.

Diffusion is defined by USEPA as “the movement of suspended or dissolved particles (or molecules) from a more concentrated to a less concentrated area. The process tends to distribute the particles or molecules more uniformly” (USEPA 2012). Diffusion will occur once a concentration gradient is present, transporting a contaminant from a zone of higher concentration to one of lower concentration.

## 3.0 Site-Specific COPCs

The following sections summarize key characteristics of the COPCs identified in the RI Report.

### 3.1 PVOCs

#### 3.1.1 Benzene

Benzene has the lowest  $K_{oc}$  value of the four (4) BTEX compounds (60-83), with a relative rate of migration in groundwater that is faster than the other BTEX components. Groundwater initially migrating through sediment with BTEX present at equal concentrations will leach higher concentrations of benzene, resulting in benzene as

the BTEX component typically found at the leading edge of a leachate plume. Additionally, because of these solubility differences, the source area would be expected to become depleted of benzene more rapidly than the other compounds, and the relative concentration of benzene to the other components in the groundwater will decline with time (Agency for Toxic Substances and Disease Registry [ATSDR] 1995).

Benzene also has a high affinity for the vapor phase due to its large vapor pressure (75 mm Hg at 20° C) and HLC ( $5.5 \times 10^{-3}$  atm-m<sup>3</sup>/mol at 25° C), which determines the magnitude of partitioning between water and air (ATSDR 2007b). Benzene in surface water is likely to volatilize into the atmosphere where it will degrade through reactions with hydroxyl radicals. Benzene in sediment will readily leach to groundwater. The low density of benzene will facilitate its migration to the air/water interface, enhancing volatilization at the surface. The half-life of benzene in surface water (25° C at a depth of 1m) is estimated to be 4.8 hours and the half-life in groundwater can reach up to one (1) year.

Benzene at the OUs is expected to leach into groundwater and migrate to surface water. Once in the Chicago River system, benzene will be subject to volatilization as it has been shown to have a half-life of 2.7 h in river model with a depth of 1 m, stream velocity of 1 m/sec, and a wind velocity of 3 m/sec at 20 °C (Jorgensen & Fath 2010).

### **3.1.2 Ethylbenzene**

Ethylbenzene has the highest  $K_{OC}$  value of the four (4) BTEX compounds (622), resulting in a relative rate of migration in groundwater that is slower than the other BTEX components. It is still considered to have moderate mobility in soils and sediments. Sorption and retardation by sediment organic carbon content will occur to a moderate extent. In soils and sediments with low organic carbon content, adsorption will not be a significant pathway and ethylbenzene will tend to leach into groundwater (ATSDR 1995).

The high HLD of ethylbenzene ( $6.6 \times 10^{-3}$  atm-m<sup>3</sup>/mol at 25° C) indicates that a significant proportion will partition from water into air. Ethylbenzene dissolved in surface water will thus migrate into the atmosphere. Since it has a moderately high vapor pressure (7 mm Hg at 20° C), ethylbenzene can also evaporate fairly rapidly from dry soil. Like benzene, atmospheric reaction with hydroxyl radicals can limit the atmospheric transport of ethylbenzene. The volatilization half-life of ethylbenzene in a constructed wetland located in Phoenix, Arizona ranged from approximately 40 to 200 hours. Like benzene, ethylbenzene does not significantly bioaccumulate in aquatic food chains in comparison to chemicals such as organochlorine pesticides (ATSDR 2010).

In water, ethylbenzene is more likely to evaporate and be biodegraded. It will evaporate rapidly from the surface of moving and shallow water with a half-life for evaporation of 3.1 hours in the model river described in the Benzene section above. Ethylbenzene does not readily hydrolyze, but it may be adsorbed by sediment. Ethylbenzene is likely to be adsorbed moderately by soil and sediment, and it is likely to leach from sediment to groundwater (ATSDR 2010). It is reported that ethylbenzene can be completely degraded in groundwater in 8 days.

### **3.1.3 Toluene**

The major transport mechanism for toluene in water is evaporation. Toluene in surface water tends to evaporate due to its high vapor pressure. Toluene tends to leach from sediment to groundwater and surface water due to its low  $K_{OC}$  (182). Its transportation from sediment to groundwater and surface water will depend on sediment composition. A higher portion of toluene will adsorb to sediments with high levels of organic material, while toluene in sandy sediments more likely to migrate to groundwater and surface water. Toluene in groundwater is not readily biodegraded, but will tend to evaporate to the atmosphere (ATSDR 2017).

### **3.1.4 o, Xylene, m and p Xylene, and Total Xylenes**

Xylenes are mobile in sediments and will not strongly adhere to organic matter due to their  $K_{OC}$  values of up to 383. Xylenes are expected to volatilize from surface water, based on their HLCs (0.005–0.007 atm-m<sup>3</sup>/mol) and vapor pressures (6.6–8.8 mm Hg). Surface volatilization is also exacerbated if the soil is moist. The volatilization half-life of o-xylene from a model river is reported to be 5.6 hours. Long-range atmospheric transport is not likely to be a significant process for xylenes as they quickly undergo photooxidation (ATSDR 2007d).

### 3.1.5 1,2,4- Trimethylbenzene

1,2,4-Trimethylbenzene tends to moderately adsorb to soil and sediment due to their estimated  $K_{oc}$  values of 614. Volatilization is a major route of removal however, and will rapidly occur from both soil and water surfaces as predicted by a HLC of  $5.18 \times 10^{-3}$  and vapor pressure of 2.03 mm Hg. The volatilization half-life of 1,2,4-trimethylbenzene from a model river is reported to be 3.4 hours. Degradation of 1,2,4-trimethylbenzene in the atmosphere occurs through reactions with hydroxyl radicals, with half-life estimates of 1,2,4-trimethylbenzene in the atmosphere of approximately 6 hours (USEPA 1987). At the North Branch River site, 1,2,4-trimethylbenzene would be expected to volatilize to the atmosphere, if transported from sediment to surface water.

## 3.2 Polycyclic Aromatic Hydrocarbons

Physicochemical properties of PAHs, such as water solubility, vapor pressure, HLC,  $K_{oc}$ ,  $K_{ow}$ , can be reliable predictors of their environmental fate and transport. Some of these transport and partitioning characteristics are also roughly correlated to their molecular weights, and can therefore be then be used to group PAHs as follows:

- Low molecular weight compounds - 152-178 g/mol
- Medium molecular weight compounds - 202 g/mol
- High molecular weight compounds - 228-278 g/mol

PAHs with two (2) to three (3) rings are present in air predominantly in the vapor phase. PAHs that have four (4) rings exist both in the vapor and particulate phase, and PAHs having five or more rings are found predominantly in the particle phase (ATSDR 1995).

### 3.2.1 Low Molecular Weight PAHs

Low molecular weight PAHs (1-methylnaphthalene, 2-methylnaphthalene, and naphthalene) have  $K_{oc}$  values in the range of  $10^3$  to  $10^4$ , indicating a moderate potential to be adsorbed to organic carbon in the soil and sediments. For example, naphthalene can be moderately adsorbed with the extent dependent on the organic carbon content. This adsorption will only somewhat retard naphthalene's groundwater transport. In an estuary, volatilization and biodegradation are the major removal processes for low molecular weight compounds (Readman et al. 1982). Biodegradation of naphthalene in soil occurs primarily under aerobic conditions, while abiotic degradation seldom occurs in soils (ATSDR 2005).

The percentage of low molecular weight PAH compounds that migrate into groundwater tend to be removed from the water column by volatilization to the atmosphere. Low molecular weight PAHs have HLCs in the range of  $10^{-3}$  to  $10^{-5}$  atm-m<sup>3</sup>/mol, indicating significant volatilization from water. These PAHs may be substantially removed by volatilization under suitable conditions (high temperature, low depth, high wind). As an example, an estimated volatilization half-life of anthracene in a stream with moderate current and wind is roughly 18 hours, versus approximately 300 hours in a body of water with a depth of 1 meter and no current (Southworth et al. 1979). The most significant atmospheric removal process for naphthalene is reaction with photochemically produced hydroxyl radicals (Howard 1989). The rate for this reaction is  $2.17 \times 10^{-11}$  cm /molecule-sec (Atkinson et al. 1987) and the atmospheric half-life for naphthalene based on this reaction is less than 1 day. Volatilization from soil may also be a substantial loss mechanism. Volatilization was found to account for about 30% of loss of naphthalene in soil (ATSDR 2005). A moderate amount of low molecular PAHs at the South Station and Throop Upland OUs will be expected to migrate into the South Branch of the Chicago River. Once in the Chicago River system, a good portion of these PAHs will volatilize from sediment or groundwater to then react with hydroxyl radicals in the atmosphere.

Naphthalene has been found in the soil gas and indoor air at South Station. Wet or dry deposition can bring naphthalene from atmosphere to surface water or soil. Based on its vapor pressure of 0.085 mm Hg at 25 °C, naphthalene in dry soil tends to volatilize to atmosphere or soil vapor. With a log octanol-water partition coefficients ( $K_{ow}$ ) for naphthalene of 3.3, only a small fraction of naphthalene is expected to be associated with particulate matter and benthic sediments, while most of the naphthalene will be retained in solution. The half-life of naphthalene in surface water and soil is short since it tends to volatilize and be biodegraded. Similar with

what happens in surface water, naphthalene in soil tends to volatilize to soil vapor or the atmosphere and a moderate fraction of naphthalene will be adsorbed by solid, which depends on the organic carbon content of the soil. Because of its low  $K_{OW}$  value, naphthalene will readily transport through groundwater (ATSDR 2005).

### **3.2.2 High Molecular Weight PAHs**

The high molecular weights that drive the physiochemical properties of these compounds generally result in low water solubility rates and a high affinity for organic carbon (ATSDR 1995). High molecular weight PAHs (benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, dibenz(a,h)anthracene, indeno(1,2,3-cd)pyrene) have  $K_{OC}$  values in the range of  $10^5$  to  $10^6$ , indicating a greater tendency to adsorb to organic carbon. This sorption tendency also increases with greater surface area of the sorbent particles. For example, pyrene adsorption coefficients have been shown to increase with sediment media of greater surface area as follows: sand 9.4 to 68; silt 1,500 to 3,600; and clay 1,400 to 3,800 (Karickhoff et al. 1979).

Because of their strong tendency to sorb to organic matter, high molecular weight PAHs are much less likely to leach into groundwater and surface water, and then vaporize into the atmosphere. As an example, Hattemer-Frey and Travis (1991) found that the low solubility, low vapor pressure and high  $K_{OW}$  of benzo(a)pyrene result in its partitioning mainly between soil (82%) and sediment (17%), with  $\approx 1\%$  partitioning into water and  $<1\%$  into air, suspended sediment and biota. Of the small percentage of high molecular weight PAHs that are found in aquatic systems, approximately two-thirds are adsorbed to particles that either have settled to the bottom or are suspended in the water column, and only about one-third are present in dissolved form (Eisler 1987). These PAHs were found to have lower settling fluxes in the water column of Lake Superior, being efficiently buried in the surficial sediments with little recycling (Baker et al. 1991).

High molecular PAHs have HLCs in the range of  $10^{-3}$  to  $10^{-5}$  atm-m<sup>3</sup>/mol, meaning that they volatilize from water only to a limited extent. Half-lives for volatilization of benzo(a)anthracene and benzo(a)pyrene from water have been estimated to be greater than 100 hours (Southworth 1979). Other processes, such as adsorption, photolysis, or biodegradation may become more important than volatilization in slow-moving, deep waters. The majority of high molecular weight PAHs at the North Branch River site will be expected to adsorb to organic matter in the sediment.

### **3.3 Polychlorinated Biphenyls**

PCB are persistent chemicals and do not readily break down in the environment. They can remain in the environment for long periods of time, cycling between soil, sediment, water, and the atmosphere, and can migrate long distances.

Atmospheric transport is the most important mechanism for global transport of PCBs. This is supported by the estimated HLCs for Aroclors and PCB congeners, which range from  $10^{-4}$  to  $10^{-3}$  atm-m<sup>3</sup>/mole and  $10^{-5}$  to  $10^{-4}$  atm-m<sup>3</sup>/mole, respectively. PCBs in the atmosphere, both in the vapor phase and sorbed to particles, are the result of volatilization from soil and water surfaces. PCBs with vapor pressures greater than  $10^{-4}$  mm Hg appear to exist in the atmosphere almost entirely in the vapor phase, while PCBs with vapor pressures less than  $10^{-8}$  mm Hg appear to exist almost entirely in the adsorbed phase, and PCBs with between  $10^{-4}$  and  $10^{-8}$  mm Hg exist in both the adsorbed and vapor phase. PCBs are removed from the atmosphere by wet deposition of aerosols and vapors, dry deposition of aerosols, or vapor adsorption to water, soil, and plants (ATSDR 2000 and 2011).

PCBs in surface water exist in dissolved, particulate and colloid-associated phases, and are transported by diffusion. Microorganisms in sediments can uptake PCBs, and the PCBs are bioaccumulated within them. Since conditions at the North Branch River site aren't expected to support an active biological community, uptake from microorganisms is not expected to be significant. At the North Branch River site, PCBs are primarily sorbed to sediment particles that may become suspended into the surface water and, to a lesser extent, may dissolve into groundwater and migrate to surface water.

### **3.4 Inorganics**

Adsorption, precipitation, coprecipitation, and complexation are processes that affect the fate and transport of metals in the environment. The adsorption of heavy metals to sediment is largely site-specific, affected by pH, oxidation-reduction potential, the ionic strength of the water, the concentration of complexing ions, and the

species and concentration of the metal. In addition, the fate of heavy metals in aquatic systems depends on partitioning between soluble and particulate solid phases. The behavior of these metals is typically dependent on their speciation. Some species become more soluble when formed, while other forms precipitate and settle out of water columns or groundwater. The extent of metal adsorption under equilibrium conditions is typically characterized by the distribution coefficient,  $K_d$ , which measures the equilibrium partitioning ratio of adsorbed to dissolved contaminants (ATSDR 2007a).

#### **3.4.1 Arsenic**

Arsenic in soil may be transported by wind or in runoff or may leach into the subsurface soil. In sediment, arsenic can sorb to the sediment particles and can be transported by dispersion of the sediment or by leaching to the groundwater. Because many arsenic compounds tend to partition to soil or sediment under oxidizing conditions, leaching usually does not transport arsenic to any great depth. Since leaching of arsenic is correlated with organic carbon content, downward migration has been shown to be greater in sandy soil and sediment than in soil and sediment with higher fractions of clay. In addition to the percentage of clay and organic matter in soil and sediment, the iron oxide content and pH also have a significant influence on arsenic adsorption. Arsenic adsorbed to iron or manganese oxides may be released under reducing conditions when in sediment or flooding circumstances. Dissolution may also occur due to microbial action when nutrient levels are adequate (ATSDR 2007a).

Transport and partitioning of arsenic in water depends upon the chemical form (oxidation state and counter ion) of the arsenic, as well as interactions with other materials present. Under oxidizing and mildly reducing conditions, groundwater arsenic concentrations are usually controlled by adsorption rather than by mineral precipitation. In acidic and neutral waters, arsenate (a common oxidation state of arsenic) is more strongly adsorbed relative to arsenic. In high-pH waters (i.e., pH greater than 9) aquifer  $K_d$  values are considerably lower for both oxidation states. Once in a river system, arsenic may also be adsorbed from water onto organic material, iron oxides, aluminum hydroxides, and manganese compounds in sediments. Soluble forms however, may be transported long distances (ATSDR 2007a).

In both oxidizing and reducing groundwater, oxyanions or thiooxyanions are the two (2) major forms of inorganic arsenic. Arsenic may co-precipitate with other common soil and sediment minerals such as iron oxides and iron sulfides in groundwater with iron oxides playing a significant role in oxidizing environments and sulfides in reducing environments. In aqueous systems, arsenic mobility can be altered by microbial interactions resulting in the conversion of inorganic arsenic between its oxidized or reduced oxyanionic forms and methylation-demethylation of arsenic (USEPA 2007).

#### **3.4.2 Aluminum**

Aluminum in this elemental state cannot be degraded in the environment but may be involved various precipitation or ligand exchange reactions. The only one (1) oxidation state of aluminum is Al (III), and Al (III) will not be oxidized or reduced under environmental conditions. The presence of different ligands in the environment such fulvic and humic acids can complex aluminum. In environment, the transport and partitioning of aluminum depends on the pH values, its chemical properties and the presence of acid or ligands. The adsorption of aluminum on suspended solids is promoted by the increasing levels of suspended solid in aqueous phase, but the adsorption curve would not be linear (ATSDR 2008).

#### **3.4.3 Chromium**

Chromium is present in the environment primarily in particulate form. Key soluble forms are chromium(VI) and chromium(III), with chromium(VI) being the more soluble, mobile, and toxic to living organisms. Chromium(III) has low solubility and reactivity, which result in low mobility and low toxicity. Chromium is primarily present in soil and sediment as an insoluble oxide and is not very mobile. Results from leachability investigations indicate that chromium has an initial period of mobility before forming insoluble complexes that do not migrate easily. Similar to aquatic environments, soluble chromium(VI) and chromium(III) account for a small percentage of the total chromium. Chromium(VI) and chromium(III) are more mobile in soil, the degree of which is dependent on the sorption characteristics of the soil or sediment. Transport of chromium occurs mainly through surface runoff and leaching into groundwater. The leachability of soluble and unabsorbed chromium(VI) increases with



increasing soil pH. However, soluble forms (chromium[VI]) are expected to convert to insoluble forms (chromium[III]) in organic matter (ATSDR 2012).

Most of the chromium released into water will ultimately be deposited in the sediment, with soluble chromium(III) accounting for a very small percentage of the total chromium. Chromium(III) occurs mostly as suspended solids adsorbed onto clayish materials, organics, or iron oxide ( $\text{Fe}_2\text{O}_3$ ) present in water. In the Amazon and Yukon Rivers, only about 10.5–12.6% of chromium is in solution, the rest being present in the suspended solid phase. Chromium(VI) will likely reduce through intramedia transport to chromium(III) by organic matter in water. Chromium compounds do not volatilize from water to the atmosphere, meaning that its fate is typically deposition in sediments (ATSDR 2012).

#### **3.4.4 Copper**

The valence states of copper complexes may be +1, +2, +3, and +4, among which, copper (III) and (IV) complexes are rare and unstable in water and copper (II) complexes are main soluble complexes for copper in aquatic environments. Copper will be stable over a wide range of geochemical conditions in the solid phase of soils and sediment materials based on its solubility and sorption behavior. Copper in groundwater is expected to be associated with colloids that appear to be organic in nature (USEPA 2007).

#### **3.4.5 Lead**

Lead transport in soil and sediment is a function of adsorption at mineral interfaces, the precipitation of sparingly soluble solid forms of the compound, and the formation of relatively stable organic-metal complexes or chelates with soil organic matter. Lead is typically strongly sorbed to organic matter in soil and sediment, although it may enter surface waters as a result of the erosion of lead-containing soil and sediment particulates. This process is dependent on multiple factors such as soil pH, soil type, particle size, organic matter content of soil, the presence of inorganic colloids and iron oxides, cation exchange capacity, and the amount of lead in soil. The downward movement of elemental lead and inorganic lead compounds from soil and sediment to groundwater by leaching is very slow under most natural conditions except for highly acidic situations that enhance the solubility of lead. In soils with pH greater than or equal to 5 and with at least 5% organic matter content, lead is retained in the upper 2 to 5 cm of undisturbed soil where it is bound into crystalline matrices of rocks and essentially immobile. At a pH of 4 to 6, dissolved lead in ionic form ( $\text{Pb}^{2+}$ ) and ion pairs (e.g.,  $\text{PbSO}_4$ ) are the predominant species that become soluble and leach out (ATSDR 2007c).

A significant fraction of lead carried by river water is expected to be in an undissolved form, which can consist of colloidal particles or larger undissolved particulate matter containing lead carbonate, lead oxide, or lead hydroxide. The ratio of lead in suspended solids to lead in dissolved form varies depending on the waterway, from as little as 4 to 1 in rural streams to as high as 27 to 1 in urban streams (ATSDR 2007c).

#### **5.4.4.6 Mercury**

There are three (3) oxidation states of mercury:  $\text{Hg}^0$  (metallic),  $\text{Hg}_2^{2+}$  (mercurous), and  $\text{Hg}^{2+}$  (mercuric- $\text{Hg}(\text{II})$ ).

In the atmosphere, elemental mercury vapor is the dominant species and will remain in the atmosphere until atmospheric conversion to divalent species or uptake and retention by plant leaves and the subsequent deposition as divalent species in litterfall (USEPA 1997).

Once deposited in soil,  $\text{Hg}(\text{II})$  species tend to form inorganic  $\text{Hg}(\text{II})$  compounds such as  $\text{HgCl}$ ,  $\text{Hg}(\text{OH})$  and inorganic  $\text{Hg}(\text{II})$  compounds complexed with organic anions under typical soil conditions (e.g., pH, temperature and soil humic content). Inorganic  $\text{Hg}(\text{II})$  compounds are quite soluble (and, thus, theoretically mobile) but they form complexes with soil and sediment organic matter (mainly fulvic and humic acids) and mineral colloids; the former is the dominating process. The complexing behavior greatly limits the mobility of mercury in soil and thereby reduces mercury partitioning to runoff. The  $\text{Hg}(\text{II})$  and methylmercury complexes in soil can be theoretically translocated by plant resulting in transfer through the terrestrial food chain but the uptake from ordinary soils, especially to above-ground parts of plants, appears to be insignificant (USEPA 1997).

Mercury can enter the freshwater environment through a number of pathways:  $\text{Hg}(\text{II})$  and methylmercury from atmospheric deposition (wet and dry) can enter water bodies directly;  $\text{Hg}(\text{II})$  and methylmercury can be transported to water bodies in runoff (bound to suspended soil/humus or attached to dissolved organic

carbon); or Hg(II) and methylmercury can leach into the water body from groundwater flow in the upper soil layers. In the freshwater system, the same complexation and transformation processes that occur to mercury species in soil will occur along with additional processes due to the aqueous environment (Gworek et al. 2016).

#### **5.4.4.7 Nickel**

There are many adsorbing species in soil, and many factors affect the extent to which nickel is adsorbed such as soil texture, bulk density, pH, organic matter, the type and amount of clay minerals, hydroxides, and extent of groundwater flow. In general however, nickel is strongly adsorbed by soil. Nickel sorption is most influenced by soil pH, and to a lesser extent clay content and the amount of hydrous iron and manganese oxides. In acidic soil,  $\text{Ni}^{2+}$  is the predominant species in solution.  $\text{NiOH}^+$  is the predominantly adsorbed species in alkaline soils, limiting the mobility of nickel as adsorption is almost irreversible (ATSDR 2005b).

The majority of the nickel released into waterways is associated with particulate matter and is transported until settling in areas of active sedimentation such as the mouth of a river. Adsorption of nickel onto suspended particles in water is one (1) of the main removal mechanisms of nickel from the water column. Nickel is strongly adsorbed at mineral surfaces such as oxides and hydrous oxides of iron, manganese, and aluminum. Such adsorption plays an important role in controlling the concentration of nickel in natural waters (ATSDR 2005b).

#### **5.4.4.8 Zinc**

Zn (II) is the predominant oxidation state of zinc in the environment. In natural water, zinc has the tendency to partition into sediment through sorption onto hydrous iron and manganese oxides, clay minerals, and organic materials, during which process pH, concentrations of the substance, oxidation-reduction potential, salinity, and cation exchange capacity may play important roles. In general zinc tends to be more soluble and mobile under acid condition while tends to be insoluble and immobile under alkaline condition. Although zinc is an essential nutrient for all organisms, biodegradation of zinc seems less significant in soil and sediment than in water phase (ATSDR 2005c).

#### H.4 REFERENCES

- Agency for Toxic Substances and Disease Registry (ATSDR). 1995. *Toxicological profile for Polycyclic Aromatic Hydrocarbons (PAHs)*. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.
- Agency for Toxic Substances and Disease Registry (ATSDR). 2005. *Toxicological profile for Naphthalene, 1-Methylnaphthalene, and 2-Methylnaphthalene*. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service <http://www.atsdr.cdc.gov/toxprofiles/tp67-c6.pdf>
- Agency for Toxic Substances and Disease Registry (ATSDR). 2007a. *Toxicological profile for Arsenic*. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.
- Agency for Toxic Substances and Disease Registry (ATSDR). 2007b. *Toxicological profile for Benzene*. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.
- Agency for Toxic Substances and Disease Registry (ATSDR). 2007c. *Toxicological profile for Lead*. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.
- Agency for Toxic Substances and Disease Registry (ATSDR). 2007d. *Toxicological profile for Xylenes*. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.
- Agency for Toxic Substances and Disease Registry (ATSDR). 2010. *Toxicological profile for Ethylbenzene*. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.
- Agency for Toxic Substances and Disease Registry (ATSDR). 2012. *Toxicological profile for Chromium*. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.
- Atkinson R, Arey J, Zielinska B, et al. 1987. *Kinetics and products of the gas-phase reactions of OH radicals and N<sub>2</sub>O<sub>5</sub> with naphthalene and biphenyl*. Environ Sci Technol 21:1014-1022.
- Baker, J.E., Eisenreich, S.J., and B.J. Eadie, 1991. *Sediment trap fluxes and benthic recycling of organic carbon, polycyclic aromatic hydrocarbons, and polychlorobiphenyl congeners in Lake Superior*. Environ Sci Technol 25 (3):500-509.
- Eisler R. 1987. *Polycyclic aromatic hydrocarbon hazards to fish, wildlife, and invertebrates: A synoptic review*. Laurel, MD: US Fish and Wildlife Service, Patuxent Wildlife Research Center.
- Hattemer-Frey HA, Travis CC. 1991. Benzo-a-Pyrene: *Environmental Partitioning and Human Exposure*. Toxicology and Industrial Health 7(3).
- Howard PH. 1989. *Handbook of environmental fate and exposure data for organic chemicals*. Vol. 1. Lewis Publishers, 408-421.
- Jorgensen, E. (2010). *Ecotoxicology*, Elsevier Science.
- Karickhoff SW, Brown DS, Scott TA. 1979. *Sorption of hydrophobic pollutants on natural sediments*. Water Res 13:241-248.
- Lyman, W. J., W. F. Reehl, and D. H. Rosenblatt. 1990. *Handbook of Chemical Property Estimation Methods*. American Chemical Society. Washington, D.C.
- Readman JW, Mantourar RFC, Rhead MM, et al. 1982. *Aquatic distribution and heterotrophic degradation and polycyclic aromatic hydrocarbons in the Tamar Estuary, England, UK*. Estuarine Coastal Shelf Sci 14:369-389.
- Schwertmann U, 1991. *Solubility and dissolution of iron oxides*. Plant and Soil 130:1-25.
- Southworth GR, Beauchamp JJ, Schmeider PK. 1978. *Bioaccumulation potential of polycyclic aromatic hydrocarbons in Daphnia pulex*, Water Res 12:973-977.

- United Kingdom Environment Agency, U.K. Environment Agency, 2013, ISBN : 1844320669, *An Illustrated Handbook of DNAPL Transport and Fate in the Subsurface*.
- United States Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, HHS, November 2000, *Toxicological Profile for Polychlorinated Biphenyls (PCBs)*.  
<https://www.atsdr.cdc.gov/toxprofiles/tp17.pdf>
- United States Environmental Protection Agency, USEPA, EPA600/4.79.032. 1979, *Determination of Octanol/Water Distribution coefficients, Water Solubilities, and Sediment/Water Partition Coefficients for Hydrophobic Organic Pollutants*.
- United States Environmental Protection Agency, USEPA, EPA/540/4-90/053, October 1990, *Basic Concepts of Contaminant Sorption at Hazardous Waste Sites*.  
<http://www.epa.gov/superfund/remedytech/tsp/download/issue6.pdf>
- United States Environmental Protection Agency, USEPA, EPA 749-F-94-022, 1994, *OPPT Chemical Fact Sheet on 1,2,4- Trimethylbenzene*. [http://www.epa.gov/chemfact/f\\_trimet.txt](http://www.epa.gov/chemfact/f_trimet.txt)
- United States Environmental Protection Agency, USEPA, December 1997, *Mercury Study Report to Congress, Volume III: Fate and Transport of Mercury in the Environment*.  
<http://www.epa.gov/ttn/caaaa/t3/reports/volume3.pdf>
- United States Environmental Protection Agency, USEPA, October 2007, *Monitored Natural Attenuation of Inorganic Contaminants in Ground Water Volume 2*
- United States Environmental Protection Agency, USEPA, December 2009. *Guidance for Reporting on the Environmental Fate and Transport of the Stressors of Concern in Problem Formulations*.  
[http://www.epa.gov/pesticides/science/efed/policy\\_guidance/team\\_authors/endangered\\_species\\_registration\\_workgroup/esa\\_reporting\\_fate.htm](http://www.epa.gov/pesticides/science/efed/policy_guidance/team_authors/endangered_species_registration_workgroup/esa_reporting_fate.htm)
- United States Environmental Protection Agency, USEPA, 2012, *Glossary of Technical Terms*, access date May 29, 2015 <http://www.epa.gov/oust/cat/tumgloss.htm>
- USEPA, United States Environmental Protection Agency, *Technical Factsheet on: Benzene*.  
<http://www.epa.gov/ogwdw/pdfs/factsheets/voc/tech/benzene.pdf>
- USEPA, United States Environmental Protection Agency, *Technical Factsheet on: Ethylbenzene*.  
<http://www.epa.gov/ogwdw/pdfs/factsheets/voc/tech/ethylben.pdf>
- USEPA, United States Environmental Protection Agency, *Technical Factsheet on: Toluene*.  
<http://www.epa.gov/ogwdw/pdfs/factsheets/voc/tech/toluene.pdf>
- WDNR, Wisconsin Department of Natural Resources, January 2014, *Guidance on Natural Attenuation For Petroleum Releases*. <http://dnr.wi.gov/files/PDF/pubs/rr/RR614.pdf>